

DO GLASS TRANSITIONS REPRESENT GLOBAL CHANGES TO COAL STRUCTURE?

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Introduction

At room temperature coals are glassy solids. The existence of thermal glass to rubber transitions has been claimed for coals in a number of publications. Typically, coals have glass transition temperature (T_g) in the region of 600K. There is a certain amount of contradictory experimental data published. For example, Green *et al.*¹ have presented data which suggest a second order phase transition at 573K for APCS Illinois #6 which looks like a traditional glass to rubber transition. Conversely, Lucht *et al.*² claim a second order phase transition at 655K for PSOC Illinois #6 in which the specific heat baseline is displaced downwards. It may be claimed that this difference is due to the difference in the origin of the coal but nevertheless, this raises doubts about the reproducibility of these second order phase transitions. The existence of such transitions may be important to coal processing because diffusion rates through rubbery materials are orders of magnitude faster than through the corresponding glass.

The question to be considered here is whether glass transitions represent truly global changes in the viscoelastic properties of coals. In many polymers, which have tend to have much more uniform chemical and physical structures than coal, physical properties such as Young's moduli typically reduce by two orders of magnitude³. Direct measurement of Young's moduli for coals is difficult and unreliable because of the existence of cracks and a well defined bedding plane.

The objective here is to use Differential Scanning Calorimetry (d.s.c.) to investigate thermal and solvent effected glass transitions in coals and, by comparison with another polymer system, determine whether they represent global changes to structure.

The process of quantifying glass transitions will be achieved by interpreting specific

heat (C_p) data in terms of two component Einstein C_p models. It has been shown by Merrick⁴ and Hall and Larsen⁵ that the C_p of coals from ~100K to pyrolysis temperatures can be described by Einstein C_p models that consist of two components. One component comes from easily excited atomic vibrations and has a weighting of 1/3. The second component originates from vibrations that are harder to excite and has a weighting of 2/3. C_p at any temperature, T , is given by:

$$C_p = \left(\frac{R}{a} \right) [1/3 g_1(\Theta_1/T) + 2/3 g_2(\Theta_2/T)] \quad 1$$

where $g(\Theta/T)$ is the Einstein function:

$$g = \frac{\exp(\Theta/T) (\Theta/T)^2}{(\exp(\Theta/T) - 1)^2} \quad 2$$

a is the mean atomic weight and Θ is the Einstein temperature. Equation 1 provides a two component fit to empirical C_p data, Θ_1 and Θ_2 being adjustable parameters. One advantage of Equation 1 is that it explicitly separates the mean atomic weight and the Einstein temperatures Θ . Θ is therefore independent of the chemical structure and provides a basis for comparing chemically different structures.

Hall⁶ has shown that Equation 1 provides a good description for C_p data of a Dioxane Lignin (DL) obtained by Hatakeyama *et al.*⁷. DL is a good model for certain aspects of coal structure because it is a heterogeneous aromatic-based crosslinked polymer. However, it is simpler to understand the structure of DL because there are no analogues to coal macerals, mineral matter contamination or bedding planes. The chemical structure is more uniform than coal. Hall⁶ demonstrated that Θ_2 decreased from 1630K below T_g to 1230K above T_g , a decrease of 400K. This is taken as the bench mark figure for a material that has well-defined glass to rubber transition.

Experimental

A Mettler DSC 30 was used with standard aluminium pans. A detailed experimental procedure has been described previously⁸. The only difference was that C_p errors due to convective heating at low temperatures were minimized by minimizing the volume of the pan and reference chamber using a low temperature lid. Exhaustive calibration meant that temperatures were determined to ± 0.1 K, enthalpies were determined to ± 0.01 J/g. DSC was performed at 10 K/min in a carrier of dry nitrogen.

Coals were obtained from the Argonne Premium Coal Bank. The ultimate analyses from APCS was used for calculating mean atomic weights. The coals were dried in the DSC chamber at 373K until the heat flow indicated that no water remained.

Results and Discussion

A number of coals were tested. Ten separate samples of Illinois #6 were tested. Very slight second order phase transitions were detected in two cases. In three others displacement of the Cp baseline down wards was noted, similar to the observations of Lucht *et al.*² The temperature of these transitions varied between 520K and 630K. In the other experiments there were either no second order phase transitions observed, they were too small or ambiguous. Figure 1 shows a mean of the runs, overall there are no obvious second order phase transitions. The Einstein temperatures for fresh Illinois #6 were calculated to be 380K and 1200K. In the cases where a second order phase transition resembling a glass transition was observed, the reduction in the higher Einstein temperature following a glass transition was 50K. This is much less than the change of 400K calculated for DL⁶. Our conclusions are that if genuine glass to rubber transitions do indeed exist for Illinois #6 then they do not represent global changes to structure. Differences in the behaviour are probably due to sample inhomogeneity.

Pittsburgh #8 presented different problems in the identification of a possible glass to rubber transition. Figure 2 shows a typical d.s.c. result. The dashed lines mark what may be a second order phase transition followed by what may be a slight exotherm. Another interpretation of this is that it may be a first order endotherm caused by some pyrolysis effect. On the basis of the data presented here these possibilities cannot be distinguished. The problem is that the onset of softening in high swelling coals such as Pittsburgh #8 is accompanied by the evolution of tars. This result illustrates the difficulties of using d.s.c. alone to investigate glass transitions.

Two higher rank coals, Upper Freeport and Pocahontas were also investigated. We were not able to find any evidence of glass to rubber transitions for these coals below the onset of pyrolysis.

The only situation in which we were able to produce a significant, reproducible and well defined glass to rubber transition was for Wyodak coal following heat treatment. Figure 3 shows d.s.c. for Wyodak coal dried at 373K. Run 1 is on the dry coal and Run 2 is on the same sample of coal that has been heated to 573K in the d.s.c. and cooled to room temperature. Run 1 shows a well defined endotherm at 478K and a rather broad endotherm at 430K. Run 2 shows a well defined second order phase transition at 380K.

Equation 1 has been used to model the Cp data for Run 2 both below and above the glass transition. There was not enough sample to determine the elemental composition

of the Wyodak following Run 1 and the assumption is made that there is no significant change in the mean atomic weight. This is a reasonable assumption since the weight loss on Run 1 was only 3%. Figure 4 shows that Θ_2 values of 2250K and 1850K give the best fits. In other words, Θ_2 reduces by 400K as a result of the glass transition. This is the same as previously observed for the DL. We therefore conclude that this particular glass transition represents a global change to the Wyodak structure. The reasons for this are a matter for speculation but the following discussion is at least consistent with the experimental results presented here and with what is known about the molecular structure of Wyodak coal. It is known that Wyodak has a large oxygen content and a relatively large concentration of carboxylic acid groups. The first order phase transitions in Run 1 could be caused by the dissociation of these groups. The fact that they are very much reduced in Run 2 suggests some chemical change, rather than a melting phenomenon. In the original coal these acid groups would give rise to hydrogen bonding in the coal macromolecule. When they are removed the coal may become effectively less heavily crosslinked and therefore has a well defined glass to rubber transition.

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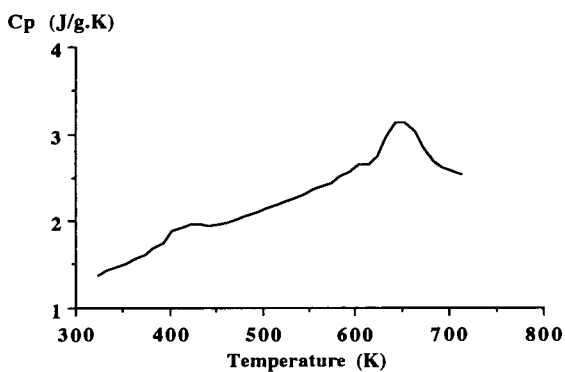


Figure 1: DSC at 10K/min for dry Illinois #6 coal.

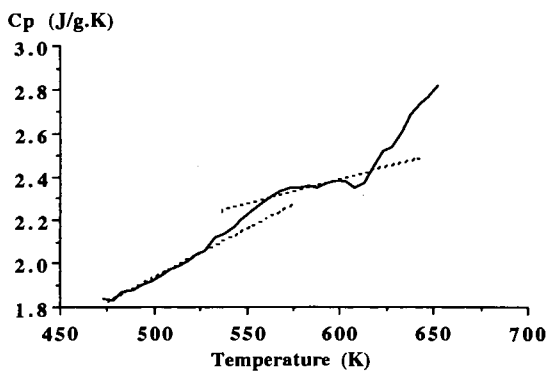


Figure 2: DSC at 10K/min for dry Pittsburgh #8 coal.

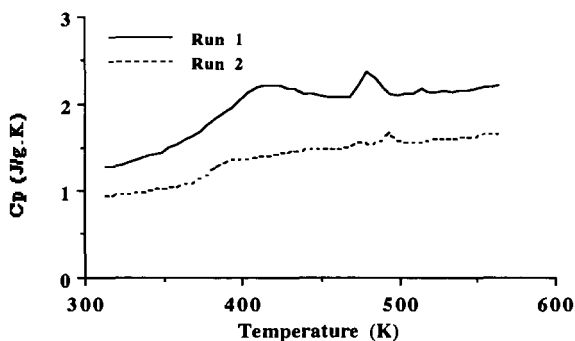


Figure 3: DSC at 10 K/min for dry Wyodak coal and a re-run of the same sample.

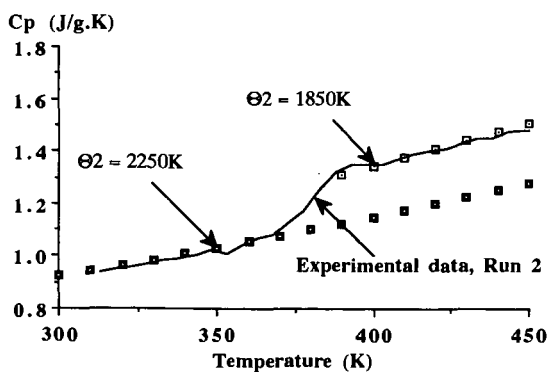


Figure 4: DSC at 10 K/min for Wyodak coal heated to 573K then cooled to room temperature together with two-component Einstein C_p theory fits to the experimental data below and above the glass transition.